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(71) Applicant: E.I. DU PONT DE NEMOURS AND
COMPANY
Wilmington Delaware 19898 (US)

(72) Inventors:
• Inaba, Akira
Yokohama-shi, Kanagawa 226 (JP)

• Oba, Takayuki
Yokohama-shi, Kanagawa 240 (JP)

(74) Representative: von Kreisler, Alek, Dipl.-Chem. et
al
Patentanwälte
von Kreisler-Selting-Werner
Postfach 10 22 41
50462 Köln (DE)

(54) Conductive paste for MLC termination

(57) The purpose of this invention is to provide a terminal electrode composition for a multiple-layered capacitor that is suitable for a plating base and that has improved resistance to heat stress as the result of sintering at a low temperature (high reliability). The terminal electrode composition for multiple-layered capacitor of this invention is made of precious metal particles and 0.5-7 wt% (based on the weight of the precious metal particles) of an inorganic binder having a 400-500°C glass transition point and a 400-550°C glass softening point.

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Description**FIELD OF THE INVENTION**

5 This invention concerns a terminal electrode composition for a multiple-layered capacitor; more specifically, this invention concerns a terminal electrode composition for a multiple-layered capacitor made of precious metal particles and an inorganic binder, and sintered at low temperature.

BACKGROUND OF THE INVENTION

10 Conventional conductive pastes made by dispersing precious metals (such as silver/palladium) and an inorganic binder dispersed in an organic binder have been used as terminal electrode materials for multiple-layered ceramic capacitors. The convention conductive paste was required to be conductive following the sintering process, to adhere to the element assembly of the capacitor before and after the sintering process, and to be made adhesive by soldering after
 15 the sintering process. A composition, having improved adhesiveness with respect to the element assembly of the capacitor before and after the sintering process, and made by combining a composition of precious metal and an inorganic binder with nickel oxide (NiO, 0.1-10 wt% based on the weight of the precious metal) was described in U.S. Patent No. 3,922,387.

20 There were various problems associated with the improvements in highly dense surface mounting techniques. In order to metalize the conventional conductive paste, sintering at 800-900°C (a comparatively high temperature, especially at 750-950°C as described in the above-mentioned U.S. Patent) was required. In the case of sintering in the above-mentioned temperature range to form a terminal electrode for the capacitor, the metal components in the paste could diffuse into the inner electrode of the capacitor, or could become sintered and could shrink in the junction of the terminal electrode and the element assembly of the capacitor, or the inorganic binder in the paste could diffuse into the element
 25 assembly of the capacitor, resulting in the generation of large inner stresses in the capacitor. As a result, rapid temperature changes generate cracking in the element capacitor assembly when soldering, or performing modification soldering onto the circuit substrate of a chip capacitor. Or in the case of a substrate that became bent due to external stresses, the capacitor could become cracked.

30 As conventional conductive pastes were subject to comparatively high temperatures in the case of using the pastes for terminal electrodes, their resistance to soldering heat stress was poor, and the circuit substrate of the chip capacitor had poor resistance to bending (poor resistance to deformation). When sintering, cracks were easily produced due to inner stresses in the element assembly of the capacitor, so that conventional conductive pastes were not reliable.

35 In the case of sintering a conventional conductive paste at 650-780°C (a comparatively low temperature), the resistance to deformation could be improved; however, poor density resulted so the other chip capacitor properties might also be impaired. The conventional conductive paste was not reliable.

The purpose of this invention is to provide a composition which can be used to form a terminal electrode, has suitable properties for use as a chip capacitor and which also has high mechanical strength and high reliability (high resistance to heat stress) for which the sintering takes place at 650-780°C (a comparatively low temperature).

40 The inventors found that in the case of using an inorganic binder having specific values for the glass transition point and glass softening point of the conductive paste, a terminal electrode having high reliability could be made by sintering at a comparatively low temperature; the invention was then completed.

SUMMARY OF THE INVENTION

45 The terminal electrode composition of this invention has a high sintering density with the capacitor due to sintering at low temperature, and has high resistance to heat stress (reliability), high mechanical strength, and good plating adhesiveness. A highly reliable capacitor can be made using the product of this invention; since the production requires a low temperature, production is economical.

50 Therefore this invention is directed to a terminal electrode composition for a multiple-layered capacitor, characterized by being made of precious metal particles and 0.5 to 7 wt% (based on the weight of the precious metal particles) of an inorganic binder having a 400-500°C glass transition point and a 400-550°C glass softening point.

DETAILED DESCRIPTION OF THE INVENTION

55 This invention involves a terminal electrode composition for a multiple-layered capacitor, and is characterized by being made of precious metal particles and 0.5-7 wt% (based on the weight of the precious metal particle) of inorganic binder having a 400-500°C glass transition point and a 400-550°C glass softening point.

Examples of precious metal particles include the following: white gold, palladium, gold, silver, ruthenium, osmium, their mixtures (two or more) and alloys. Silver is preferred. Either a spherical silver particle having a 0.05-10 μm particle size or an amorphous silver particle or a flaky silver particle (0.1-10 μm) or their mixture is especially preferred.

Neither the case of an excessively large or small particle size for the precious metal particle is preferred because the mixing properties of the precious metal particles with the inorganic binder are impaired.

The inorganic binder has a 400-500°C glass transition point and a 400-550°C glass softening point.

The glass softening point of the inorganic binder has considerable influence on the sintering temperature. In the case of a value which is too high, the inorganic binder inhibits sintering. In the case of a value which is too low, the binder accelerates sintering. In order that the composition not be excessively sintered and be suitably dense, the glass softening point is desirably 400-550°C.

Glass frits containing at least one of the following, e.g., 5-30 wt% SiO_2 ; 1-18 wt% B_2O_3 ; 35-70 wt% PbO ; at least one of the following, 1-20 wt% ZnO and CuO ; at least one of the following, 5-20 wt% Al_2O_3 , ZrO_2 and TiO_2 ; at least one of the following, 0.5-10 wt% Na_2O and Li_2O , may suitably be used as the inorganic binder having the above-mentioned properties. At least one of the following, i.e., 0.01-3 wt% Al_2O_3 , ZrO_2 , and TiO_2 may be added to the above-mentioned composition.

SiO_2 influences the glass softening point of the inorganic binder. In the case of a binder containing an excessive amount [of SiO_2], the softening point is increased. B_2O_3 decreases the viscosity of the composition, increases the wetting properties with the substrate, and accelerates sintering of the precious metal particles. PbO , Na_2O and Li_2O decrease the viscosity of the composition and increase the wetting properties with the substrate. Both ZnO and CuO increase the adhesiveness with the substrate. Al_2O_3 , ZrO_2 and TiO_2 improve the resistance to acids, resulting in improved resistance to the plating solution. A terminal electrode with balanced properties can be made by sintering in the case of using the components in the amounts of the above-mentioned ranges.

The amount of inorganic binder added is suitably 0.5-7 wt%, preferably 1-5 wt%, based on the weight of precious metal particles. If an insufficient amount of the inorganic binder is added, a sintered product with unsatisfactory density and plating-solution barrier properties results when sintering at 650-780°C (a low temperature), and poor adhesion to the element assembly of the capacitor occurs.

A fine powder having a 0.01-10 μm , preferably 0.1-3 μm , particle size is used as the inorganic binder. If a powder with a particle size which exceeds or falls short of the above-mentioned range, the mixing properties with the precious metal particles are exacerbated.

The terminal electrode can be made by dispersing the above-mentioned precious metal particles and inorganic binder in either water or an organic medium to form a paste, followed by application of the paste as a coating at the site where the terminal electrode of the multiple-layered capacitor is to be formed, then sintering at 650-780°C. After sintering, either a nickel plating is added or soldering is done to make the final terminal electrode.

An organic medium which can be completely burned at the above-mentioned sintering temperature (so that no residue resulting from incomplete sintering is present in the sintered membrane). Examples of organic media include solutions, which are usually used for pastes, and which are made by dissolving the following resins, are: rosin, cellulose derivate, acrylic resin, alkyd resin, in the following organic solvents, e.g., terpeneol; butyl carbinol; Carbitol acetate.

The amount of water or of the organic medium added is 10-70 wt%, preferably 20-40 wt%, based on the weight of precious metal particles.

An organic binder having the above-mentioned properties is used, so that the binder can fill the pores of either the sintered surface or the sintered membrane at a 650-780°C sintering temperature, and so that a suitable density for the terminal electrode results, so that good contact of the terminal electrode with the element assembly of the capacitor results, so that the melted solder does not interfere with the terminal electrode and the element assembly of the capacitor, and so that satisfactory adhesion strength of the terminal electrode to the element assembly of the capacitor and satisfactory mechanical strength (resistance to distortion) result.

The terminal electrode composition for the multiple capacitor of this invention is used as the base for either nickel plating or for soldering to maintain heat resistance. This composition is especially effective in preventing the plating solution from first getting into the terminal electrode and then into the electrode, which might otherwise occur when plating.

EXAMPLES

PREPARATION OF INORGANIC BINDER

The components required for conventional glass production or their precursors (such as H_3BO_3 for B_2O_3) were mixed together in the required ratios, then heated and melted. The component mixture was heated to the peak temperature at which the mixture melted and liquefied, then gas generation was stopped. The peak temperature was 1100-1500°C, especially at 1200-1400°C. Then, the melted component mixture was placed in cold water for abrupt cooling, then crushed using a roll mill. Samples for Application Examples 1-5, and Comparative Examples 6-12 were made.

The compositions (wt%), glass transition points, and glass softening points of each of the samples are shown in Table 1.

TABLE I

Component	Sample Number											
	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	23.0	29.2	21.8	28.0	22.3	6.0	5.4	15.5	34.0	33.0	34.0	37.5
B ₂ O ₃	8.5	5.5	11.6	8.0	19.2	12.0	12.4	9.6	3.0	-	9.5	4.8
PbO	66.0	57.0	46.0	56.0	37.5	80.6	78.1	73.4	48.0	63.0	44.0	43.6
ZnO+CuO	-	1.7	11.5	-	12.6	1.4	-	-	0.6	-	-	-
TiO ₂ +Al ₂ O ₃ +ZrO ₂	2.5	5.1	9.1	8.0	8.4	-	4.1	0.6	10.4	4.0	12.5	4.3
Na ₂ O or Li ₂ O	-	3.5	-	-	-	-	-	0.9	4.0	-	-	-
Others	-	-	-	-	-	-	-	-	-	-	-	9.8
glass transition point (°C)	415	425	470	470	490	335	370	380	450	520	515	570
glass softening point (°C)	470	475	525	525	535	365	400	415	555	570	600	625

PREPARATION OF PASTE

Flaky silver particles having a 3 μm average particle size were mixed with spherical silver particles having a 1 μm average particle size in a ratio of 60:40 (by weight), then 3 wt% (based on the weight of the silver) of inorganic binder (made in the above-mentioned 1) was added, and 25.84 wt% (based on total weight) of the organic medium was added, then all of the components were mixed using a roll mill to make the paste.

EVALUATION TEST

The paste made in the previous section was applied as a coating to an alumina substrate, then sintered at 650°C, at 690°C, at 730°C, and at 780°C to make samples for evaluation. The sintering density, the resistance to heat stress (reliability), the mechanical strength (deformation), and the plating adhesiveness were all evaluated.

The sintering density was evaluated by examining the cross section of the sintered membrane with a scanning electron microscope.

The resistance to heat stress was evaluated by the solder heat resistance test based on JIS C 5102.

The mechanical strength was evaluated by the bending test based on JIS C 5102.

The plating adhesiveness was evaluated by standard nickel plating/soldering.

The evaluation results are shown in Table II using a 5 point method (5: good, ...1: poor).

TABLE II

inorganic binder number	1	2	3	4	5	6	7	8	9	10	11	12
sintering density	4	4	4	4	4	5	5	5	2	2	1	1
resistance heat stress	4	5	5	5	5	1	2	3	1	1	1	1
mechanical strength (deformation)	5	5	4	4	4	5	5	5	3	3	2	1
plating adhesiveness	4	4	4	4	4	4	2	2	1	1	1	2

Claims

1. A terminal electrode composition for a multiple-layered capacitor, characterized by being made of precious metal particles and 0.5 to 7 wt% (based on the weight of the precious metal particles) of an inorganic binder having a 400-500°C glass transition point and a 400-550°C glass softening point.
2. The composition described in Claim 1, and containing an inorganic binder which is made of glass frits containing at least one chosen from the following, 15-30 wt% SiO, 1-18 wt% B₂O₃, 35-70 wt% PbO; at least one of the following, 1-20 wt% ZnO or CuO; at least one of the following, 5-20 wt% Al₂O₃, ZrO₂, or TiO₂; at least one of the following, 0.5-10 wt% Na₂O or Li₂O.
3. The composition described in Claim 1, and containing an inorganic binder which contains both the glass frits described in Claim 2, and at least one of the following, 0.01-3 wt% Al₂O₃, ZrO₂, or TiO₂.
4. The composition described in Claim 1, and containing silver particles having a value of 0.05-10 µm for the particle size as the precious metal particles.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 12 0398

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 16, no. 185 (E-1197), 6 May 1992 & JP-A-04 023308 (MITSUBISHI MATERIALS CORP), 27 January 1992, * abstract *	1-4	H01G4/008 H01G4/232
A	--- PATENT ABSTRACTS OF JAPAN vol. 16, no. 196 (E-1200), 12 May 1992 & JP-A-04 028110 (KYOCERA CORP), 30 January 1992, * abstract *	1,4	
A	--- PATENT ABSTRACTS OF JAPAN vol. 18, no. 527 (E-1613), 5 October 1994 & JP-A-06 188145 (KYOCERA CORP), 8 July 1994, * abstract *	1	
A	--- JEE JOURNAL OF ELECTRONIC ENGINEERING, vol. 28, no. 299, November 1991, TOKYO, JP, pages 58-62, XP000273336 HIROSHI AMANO: "Reliable Laminated Ceramic Capacitor carries Innovative External Electrodes" * page 58 - page 59 *		TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 April 1996	Examiner Goossens, A
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